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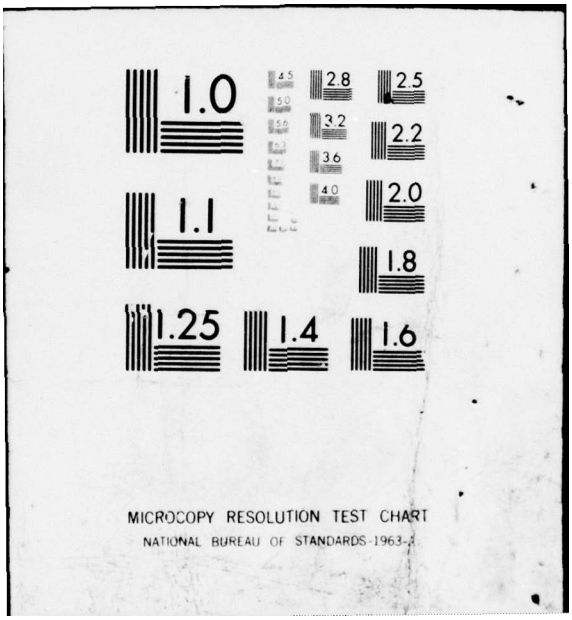
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SILICON NITRIDE LAYERS ON GALLIUM ARSENIDE BY LOW ENERGY ION BEAM SPUTTERING

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J. R. SITES

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REPORT SF14

SILICON NITRIDE LAYERS ON GALLIUM ARSENIDE BY LOW ENERGY ION BEAM SPUTTERING

Technical Report: October 1, 1978

ONR Contract N00014-76-C-0976

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L. E. Bradley

J. R. Sites

Report SF14

Department of Physics

Colorado State University

Fort Collins, Colorado, 80523

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Low energy ion beam sputtering with argon was used to deposit layers of Si_3N_4 onto GaAs for encapsulation purposes. Mechanical stability to above 900°C has been achieved; silicon diffuses into the GaAs at 600°C and above; index of refraction is a simple, but reliable test of encapsulant quality.

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SILICON NITRIDE LAYERS ON GALLIUM ARSENIDE BY LOW ENERGY ION BEAM SPUTTERING

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ABSTRACT

Silicon nitride layers are formed on gallium arsenide for encapsulation purposes. The process utilizes a 500 eV neutralized ion beam containing argon for sputtering and nitrogen for reactive deposition, directed at a pure silicon target. It is found that with proper surface preparation layers having mechanical stability to above 900°C can be formed. Photoluminescence shows that no radiative transitions are introduced in the deposition process, but that annealing inevitably leads to diffusion of silicon into the GaAs. Auger studies reveal significant oxygen impurity in the Si_3N_4, particularly near the interface. Index of refraction was found to be a sensitive, non-destructive test of encapsulant quality.

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I. INTRODUCTION

Silicon nitride has been used extensively as an encapsulant to prevent loss of arsenic when gallium arsenide is thermally annealed following ion implantation. Several techniques have been employed for the deposition of the silicon nitride layers: (1) pyrolytic or chemical vapor deposition[1-4] generally involving silane and ammonia in a nitrogen carrier gas; (2) rf plasma deposition[5,6] using nitrogen and silane; and (3) rf sputtering[7,8] with a silicon target in a 100% nitrogen atmosphere. A comparison of these techniques is found in a recent review article.[9] In general, it is concluded that Si_3N_4 layers are superior to SiO_2 and other materials for encapsulation of gallium arsenide.

In the work reported here, we have utilized low energy ion beam sputtering to deposit silicon nitride. This technique has the potential advantages of room temperature deposition and a high degree of process control.

II. EXPERIMENTAL

Deposition of the silicon nitride layers was accomplished by low energy ion beam sputtering using a pure silicon target and a 2 1/2 cm diameter beam of argon and nitrogen ions neutralized with electrons from a hot wire filament. Details of the ion beam process have been reported elsewhere.[10,11]

A stringent chemical cleaning procedure for the GaAs substrates was necessary to assure clean and reproducible surfaces. One centimeter square substrates cut from <100> GaAs purchased from Morgan Semiconductor were initially cleaned and degreased in detergent, acetone, methanol, xylene and

deionized water. Next, each was dipped in 45% hot KOH by volume for thirty seconds for oxide removal and mounted on a polishing puck for chemomechanical polishing with a Pellon pad soaked with 1% Bromine-methanol. Each substrate was screened under the 200x magnification dark field of the microscope for scratches and etch pits.

The substrates used were dipped in 50% HCl for final oxide removal, rinsed, dried, and immediately mounted in the vacuum system. During evacuation, typically to 5×10^{-7} torr, the ion source filaments were degassed with currents slightly greater than operating conditions. The argon necessary to start the ion beam was about 1×10^{-4} torr. Initially, a 500 eV Ar beam was used to sputter clean the target, a three-inch Monsanto silicon wafer, for ten minutes. Next, the GaAs substrate, in most instances, was sputter cleaned. Finally, deposition itself utilized a 1 ma/cm^2, 500 eV beam.

The amount of nitrogen added to the 1×10^{-4} torr partial pressure of argon was determined, as shown in Figure 1, by forming layers with a wide range of nitrogen pressures. The change from a silver metallic appearance for nearly pure silicon films to the blue characteristic of transparent films in the 800 Å thickness range occurred at relatively low nitrogen gas concentrations. However, the index of refraction, which was measured at 6328 Å with a Gaertner ellipsometer, continued to decline. For a nitrogen to argon gas pressure ratio greater than 3, we found a saturation in the index of refraction of the films. This saturation was interpreted as an indication of the proper gas ratio for Si_3N_4.

Post deposition annealing of the silicon nitride encapsulating layers was conducted in a quartz tube surrounded by resistive heating coils and continually flushed with hydrogen from a high quality generator. A maximum

of thirty minutes was needed for the anneal temperature to be reached after which the substrates were maintained at temperature for forty-five minutes. The system was then allowed to cool to room temperature. Typical anneal temperatures ranged from 600-950°C.

Compositional depth profiles of the silicon nitride layers were made with a Physical Electronics Auger thin film analyzer operating with a 3 kV primary electron beam. Photoluminescence studies utilized a standard set-up in which the excitation radiation was the chopped beam of a 7 mW helium-neon laser, and the emitted radiation was passed through a Jarrel-Ash 1/2 meter spectrometer to a p-i-n detector. The current output was converted to a voltage which became the input to a lock-in amplifier. In general, the sample under study was held at 20°K.

III. RESULTS

The most important parameter in determining the encapsulating quality of the silicon nitride layers is the pre-deposition substrate preparation procedure, including general cleanliness of the vacuum system. This point is illustrated in Table I where a total of 17 samples are grouped into five classes.

Class one is characteristic of a quick deposition. A substrate is not chemomechanically etched, the deposition chamber is evacuated only to the 10^{-6} torr range, and there is no substrate sputter cleaning. These parameters resulted in a very low index of refraction of 1.77, and upon annealing to 700°C, the silicon nitride showed poor adhesion.

Class two samples were typically the first sample deposited after having the deposition chamber opened to air for repairs or cleaning. The adsorbed

gases and contaminants were probably not fully pumped from the system prior to deposition. The substrates were chemomechanically cleaned, pumpdown was to the 10^{-7} torr range, and one of a variety of sputter etches was conducted. These samples had a wide range of indexes and lost adhesion anywhere from 600°C to 900°C. Figure 2b shows the affect of annealing to 600°C as compared to the preannealed silicon nitride surface (Fig. 2a). Poor mechanical adhesion results in circular holes completely covering the sample following a single anneal. It does not appear to be a gradual process.

A clean system, pumpdown to below 5×10^{-7} torr, and proper degassing is characteristic of class three, but the samples are not chemomechanically etched. Their indices of refraction were 1.93 to 1.96, and they degraded in the 700°C to 800°C range. Figure 3b shows the effects of further heat treatment to 900°C after the initial degradation at 800°C shown in Fig. 3a. The exposed GaAs has been thermally etched forming rectangular etch pits typical of <100> GaAs.

Class four samples were the first to display good resistance to annealing. They were chemomechanically cleaned and the vacuum system was properly pumped and degassed, but the samples were not sputter cleaned. The refractive index was about 2.03, whereas crystalline Si_3N_4 is reported to be 2.1.[12] Anneals to 900°C resulted in only very small etch pits from pinholes in the silicon nitride layer.

The last class is similar to class four except some kind of sputter cleaning was used. The index was much like class four and the samples repeatedly withstood annealing. Above 850°C, tiny etch pits were visible when viewed with the dark field of the microscope. The concentration of etch pits increased when the annealing was done at higher temperatures. Figure 4b shows

the surface condition after annealing to be 935°C, again in contrast (Fig. 4a) to the pre-annealed surface.

The sputter cleanings studied were combinations of nitrogen versus argon and 100 eV verses 500 eV. Although little difference in annealing behavior was found, it was felt that 100 eV nitrogen was not as effective and that 500 eV argon was superior but perhaps results in significant surface damage ($\sim$80 Å) to the GaAs.[13] There is some evidence[14] that a 100 eV argon beam sputters the surface stoichiometrically with only a few atomic layers of damage, but further work in this area should be done.

Turning now to the effects of deposition and annealing on the Si_3N_4/GaAs structures, we find that the Auger profiles before annealing are essentially as shown in Fig. 5 for both the class three and five samples pictured in Figs. 3 and 4. The important features revealed by these studies are: (1) The oxygen impurity level is relatively high, as it seems to be in other processes for depositing silicon nitride. (2) There is a particularly high concentration of oxygen close to the interface with the substrate, most likely due to partial oxidation between sputter cleaning and deposition. (3) The carbon seen is probably from the grids of the ion source and can be minimized by better alignment.

Photoluminescence studies are used to detect any radiative transition processes introduced in the GaAs during either deposition or annealing. The virgin substrate before deposition (Fig. 6) shows only exiton recombination and that due to shallow carbon acceptors. The deposition process itself (middle curve) does not add any radiative transitions. The annealing cycles, however, even as low as 600°C, introduces the double peak structure shown. The larger peak has been previously attributed[15] to a complex between a

gallium vacancy and a silicon impurity on an arsenic site, the smaller peak to the associated phonon replica. Thus, we find that even relatively modest annealing with silicon nitride encapsulants leads to a diffusion of silicon impurities into the GaAs.

IV. CONCLUSIONS

Our primary conclusion is that with reasonable care, ion beam sputtering can be used for mechanically stable silicon nitride encapsulation of gallium arsenide. There is an unexplained difficulty with excess oxygen at the interface, and there is a serious problem if diffusion of silicon dopants into the GaAs are undesirable. The latter difficulty is likely common to all deposition techniques for silicon nitride, and possibly also SiO_2, on gallium arsenide.

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TABLE I. Five classes of silicon nitride layers on GaAs substrates reflecting the effects of substrate and deposition parameters on encapsulating qualities.

Class	Chemical Etching	Vacuum System and Pumping	Sputter Cleaning	Index of Refraction	Mechanical Adhesion
1	No	Quick pumpdown	No	1.77	Poor
2	Yes	1st run	Yes	1.89±.08	Poor
3	No	Good	Yes	1.94±.02	Poor
4	Yes	Good	No	2.03±.03	Good
5	Yes	Good	Yes	2.02±.03	Good

FIGURE CAPTIONS

Fig. 1. Index of refraction and color of deposited layers as a function of nitrogen partial pressure in the bell jar.

Fig. 2. Surface of sample deposited before vacuum system had been thoroughly cleaned: (a) as deposited, (b) after 600°C anneal.

Fig. 3. Two stages of silicon nitride degradation for sample without bromine methanol treatment: (a) after 800°C anneal, (b) after 900°C.

Fig. 4. Surface of sample with chemical and sputter etch substrate preparation: (a) as deposited, (b) after 935°C anneal.

Fig. 5. Auger profile of typical sample.

Fig. 6. Photoluminescence spectrum of $1.3 \times 10^{17} cm^{-3}$ Te-doped GaAs before deposition, after deposition, and after 600°C anneal.

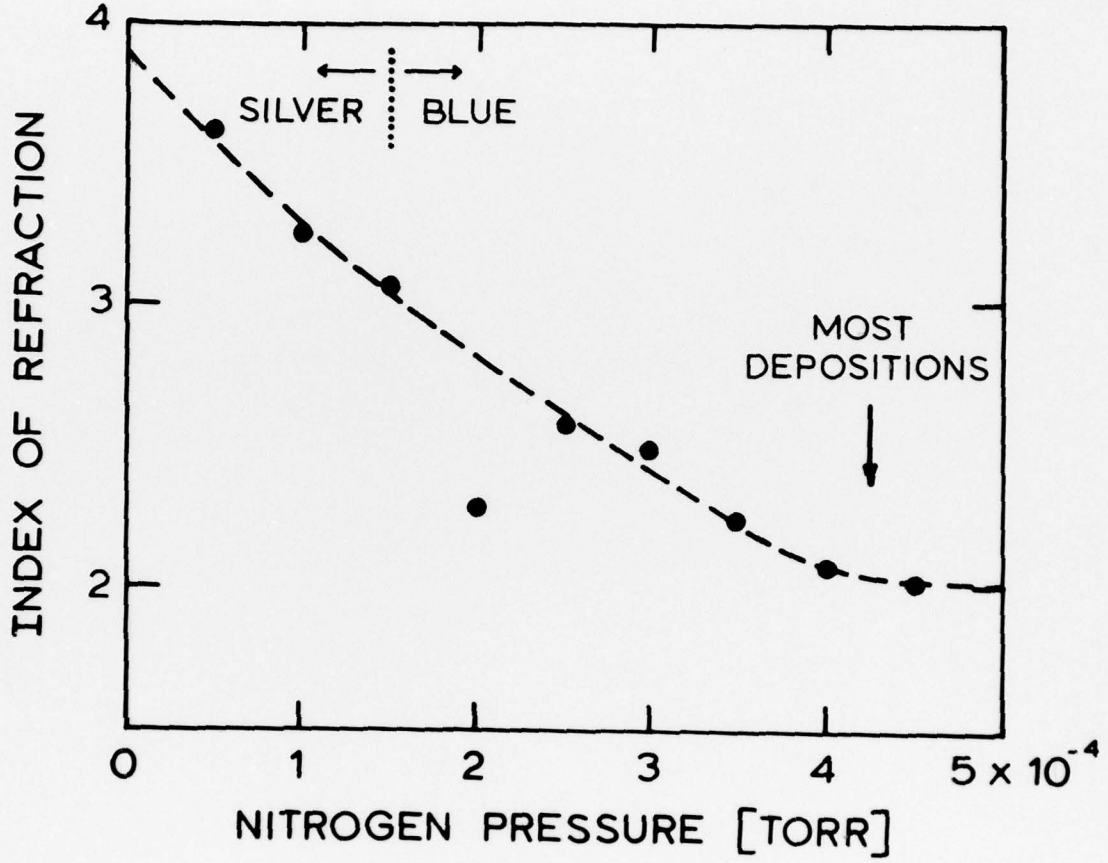
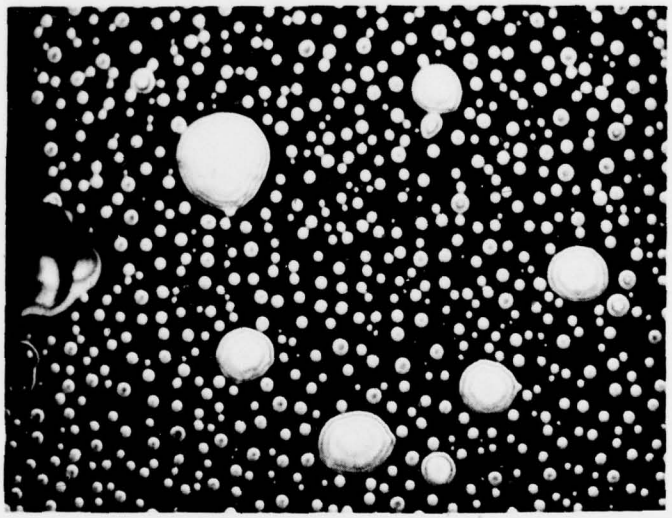

INDEX OF REFRACTION
4
3
2
SILVER
BLUE
MOST
DEPOSITIONS
0
1
2
3
4
5 x 10⁻⁴
NITROGEN PRESSURE [TORR]

Figure 1

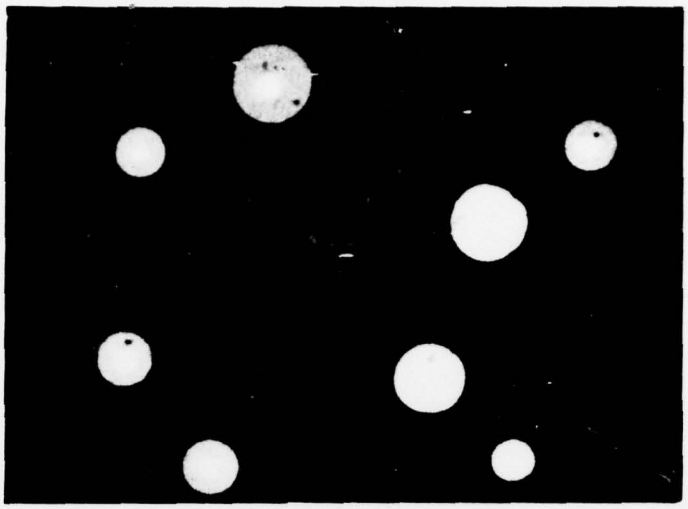
(a)



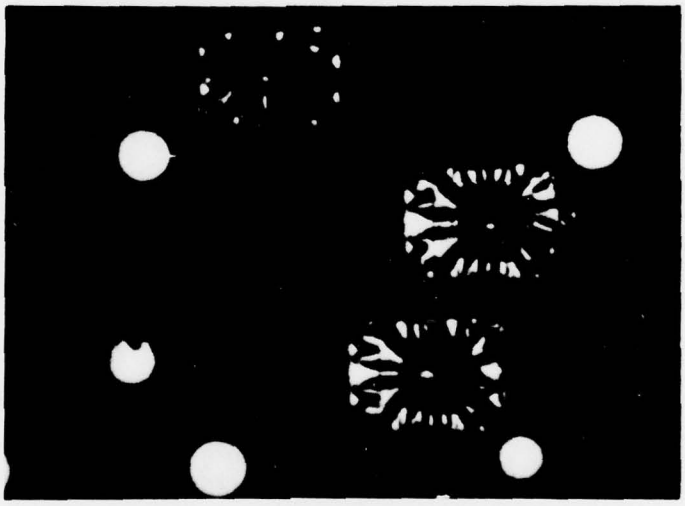
(b)

50 μm

Figure 2



(a)



(b)

50 μm

Figure 3

(a)

(b)

50 μm

Figure 4

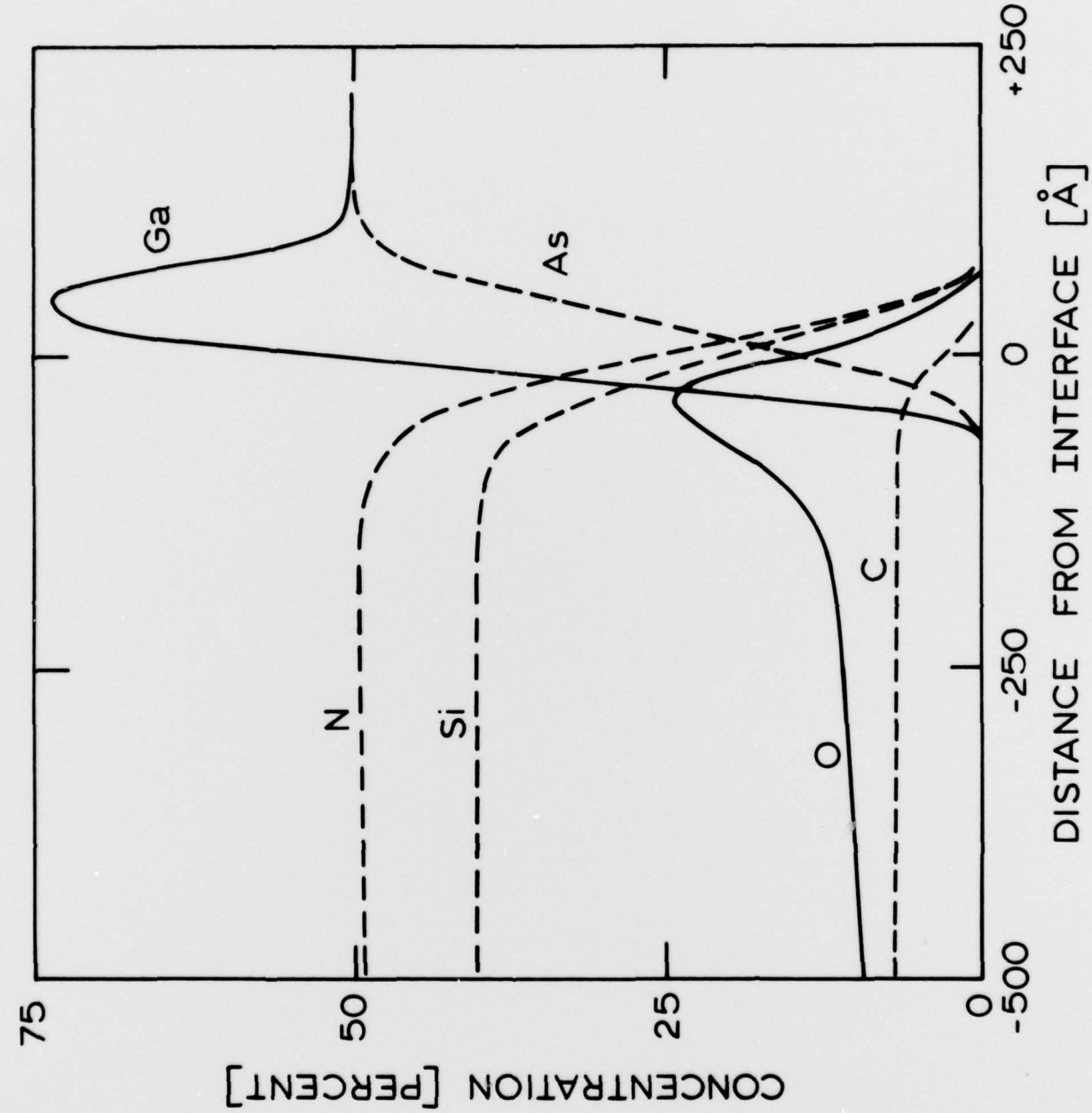

Ga
As
N
Si
O
C
75
50
25
0
-500
-250
0
+250
CONCENTRATION [PERCENT]
DISTANCE FROM INTERFACE [Å]

Figure 5

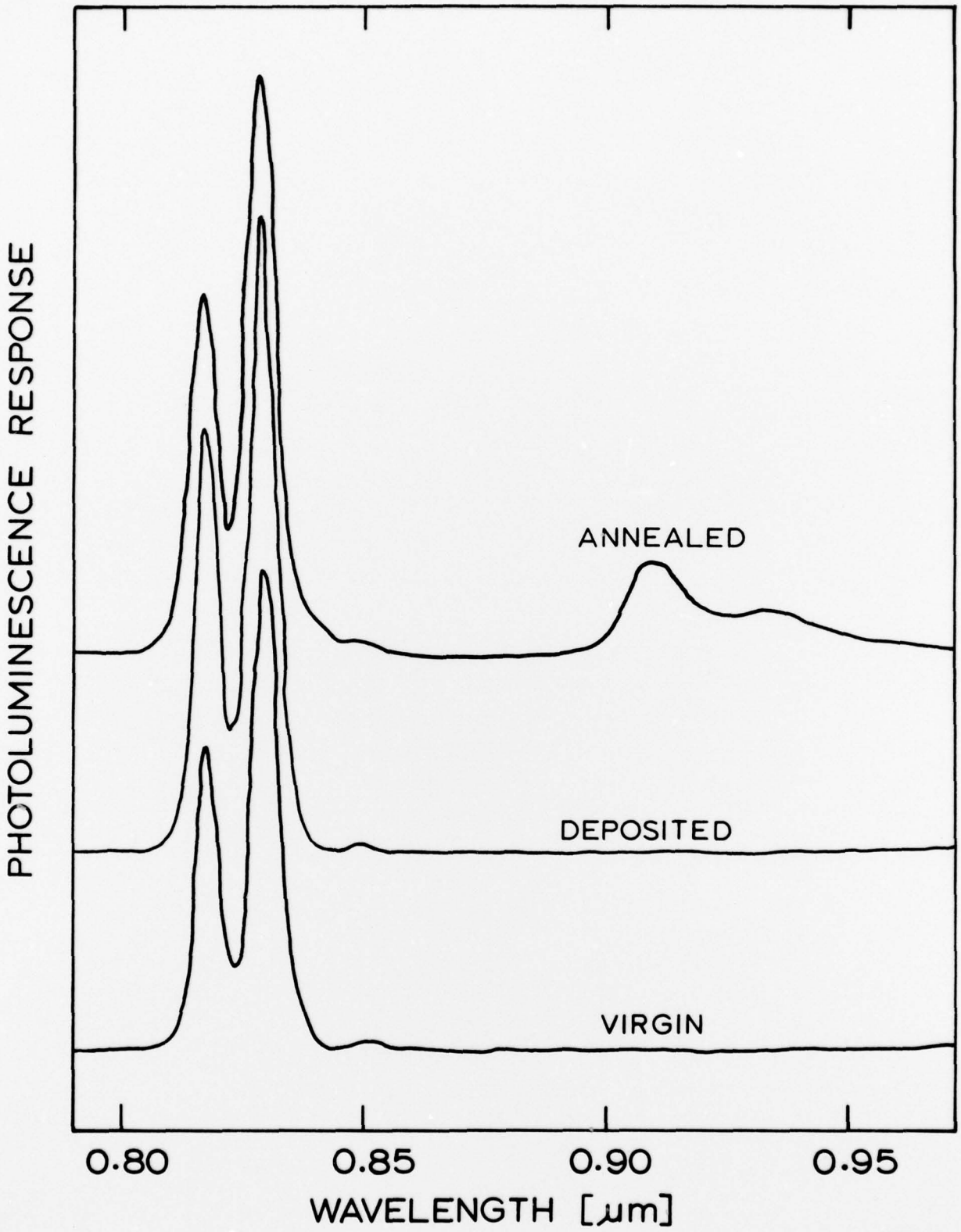

PHOTOLUMINESCENCE RESPONSE
ANNEALED
DEPOSITED
VIRGIN
0.80
0.85
0.90
0.95
WAVELENGTH [μm]

Figure 6

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